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METHODS OF ANALYSIS FOR ENAMEL AND ENAMEL RAW MATERIALS.

BY

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ROBERT D. LANDRUM,[1] Lawrence, Kansas.

Introduction. The fact that practically nothing has been published on the above subject, and the remembrance of the many long hours spent in digging out these methods and adapting them to enamels and enamel raw materials, has led the author to put them in this form for others who might use them. While he claims little originality in the methods themselves, he does claim originality in the adaptations here given. Each and every one of these methods has been thoroughly tried out, either in the laboratory of the Columbian Enameling and Stamping Company, at Terre Haute, Ind., or in the chemical laboratories of the University of Kansas.

PART I.

THE ANALYSIS OF AN ENAMEL.

The analysis of an enamel presents one of the most difficult and complicated problems with which the analyst comes in contact. An enamel is generally an insoluble silicate containing besides silica, iron, alumina, calcium, magnesium and the alkalies, generally boron, fluorine,

[1] This paper was prepared as a thesis for the master's degree at Rose Polytechnic Institute. The author desires to render thanks to Dr. W. A. Noyes and Dr. John White, his former instructors, for advice freely given, and to Dr. E. H. S. Bailey and Dr. H. P. Cady for suggestions offered. Methods, especially from the following sources, have been freely used, and adapted to the specific uses herein described: Treadwell and Hall's "Analytical Chemistry"; Classen's "Ausgewahlte Methoden der Analytischen Chemie"; Sutton's "Volumetric Analysis"; Lunge and Keane's "Technical Methods of Chemical Analysis"; "Methods of Agricultural Analysis" (Bul. 107, U. S. Dep't of Agric.); Hillebrand's "Analysis of Silicate Rocks" (U. S. Geol. Survey Bul. 305); and the files of the Journals of the various Chemical Societies.

manganese, cobalt, antimony and tin, and sometimes phosphorus and lead. Before attempting the quantitative analysis of any enamel a thorough qualitative analysis should be run, and this will enable one to choose a quantitative separation. One of the most important aids to a correct analysis is a thorough grinding. The sample should be ground to an almost impalpable powder, and every conceivable precaution for accuracy taken.

The analysis of a sample of enamel to be taken from a piece of ware involves an extra difficulty. The coating of enamel almost always consists of two or more layers—the lower a large ground coat, and the upper ones white or colored enamels. For an illuminating analysis these must be separated. The author has found the following method of V. de Luyeres[1] good for doing this: The surface is scratched lightly with a piece of emery cloth or a file, and a coating of gum acacia or glue is applied. The vessel is placed in an air-bath and heated. The glue on hardening generally carries with it some of the outer coat. The glue or gum is then broken off, dissolved in water and the enamel pieces collected on a filter paper. Some obstinate enamels require painstaking methods, such as chipping off with a chisel and separating the different coats—which always vary somewhat in color—by picking out and sorting, using a pair of forceps. A large reading glass will be useful in making these separations. Any iron from the vessel which may adhere to the enamel may be removed by means of a magnet after the sample is ground.

Analysis of an Enamel Containing Fluorine.

In an enamel containing fluorine the usual methods for silicates cannot be used, as silicon-tetra-fluoride would be volatilized in the evaporation with hydrochloric acid for the separation of the silica.

Fluorine. One gram sample is very finely ground, slowly fused with two grams each of potassium carbonate

[1] Compte Rendus 8, p. 480.

and sodium carbonate. The melt should be kept in quiet fusion over as low a flame as possible for one hour. The melt is transferred, (after cooling quickly by giving the crucible a gyratory motion while held in the tongs, causing the melt to cling to the sides instead of forming a solid cake in the bottom), to a platinum dish where it is covered with a watch glass and boiled vigorously with one hundred cc. of water. The residue is filtered off and is saved for the determination of the metallic oxides and the silica.

The covered solution is digested on a steam bath for an hour with several grams of ammonium carbonate, and on cooling more carbonate is added and the solution is allowed to stand for twelve hours. The precipitate of silica, alumina, etc., is filtered off, washed with ammonium carbonate water and is saved for further determinations.

The solution containing all the fluorine and traces of silica, phosphate, etc., is evaporated until gummy, then diluted with water and neutralized as follows: Phenolphthalein is added, and nitric acid (double normal) drop by drop until solution is colorless.

The solution is boiled and the red color which reappears is again discharged with nitric acid, boiled again and neutralized again until one cc. of acid will discharge the color.

The last traces of silica, etc., are now removed, as recommended by F. Seemann (Zeit. Anal. Chem. 44, p. 343), by the addition of 20 cc. of Schaffgotsch solution. This solution is made as follows: 250 grams of ammonium carbonate are dissolved in 180 cc. of ammonia (0.92 sp. gr.) and the solution is made up to one liter. To the cold solution 20 grams of freshly precipitated mercuric oxide are added and the solution is vigorously shaken until the mercuric oxide is dissolved.

The precipitate caused by the Schaffgotsch solution is filtered off and saved, and the solution is evaporated to dryness and the residue taken up with water.

Any phosphorus from the bone ash used in some enam-

els, and chromium which may be present, are removed from this alkaline solution by adding silver nitrate in excess. Phosphate, chromate and carbonate of silver are here thrown down and may be determined if desired.

The excess of silver is removed from the solution by sodium chloride, and one cc. double normal sodium carbonate solution is added to the filtrate, and the fluorine is precipitated by boiling with a large excess of calcium-chloride solution.

The precipitate, consisting of a mixture of calcium carbonate and fluoride, is collected on a blue ribbon filter paper and is washed, dried, ignited at low red heat, separated from the filter paper, and the residue with the ash of the paper is treated with dilute acetic acid until carbon dioxide is no longer given off on heating. The liquid is then evaporated to dryness, the residue taken up with hot water (slightly acidified with acetic acid) filtered, dried and gently ignited and weighed as CaF_2. This may be checked by heating with sulfuric acid, driving off all the excess of acid and reweighing as $CaSO_4$. This method gives results for the amount of fluorine checking within 0.2%, but which are generally from 2% to 4% low.

Silica. For the estimation of silica and the metallic oxides, first the precipitate from the Schaffgotsch mercuric oxide solution is ignited to drive off the mercuric oxide, and the silica left is weighed. The residue from the original melt, together with the precipitate obtained by ammonium carbonate (after the drying and removal from the filter paper whose ash is added) are then dissolved in hydrochloric acid. The solution is evaporated to dryness and moistened with hydrochloric acid. It is diluted with water and the silica is filtered off, weighed, and this with that previously obtained is the total silica.

Iron, Alumina and Manganese. The solution from the silica is raised to boiling and the iron and aluminum are precipitated as hydroxides. Then 5 cc. of bromine water is added and the boiling continued for five minutes.

The precipitate is dried on filter paper and ignited separately from it in a weighed platinum crucible, to which the ash of the filter-paper is afterwards added. The precipitate consists of Al_2O_3, Fe_2O_3, and Mn_2O_3, and is weighed as such. It is then fused with fifteen times its weight of potassium pyrosulfate over a low flame for three hours with the crucible covered. The crucible, contents and cover are placed in a beaker and dilute sulfuric acid (10:1) is added. By warming and continued shaking of liquid complete solution may be obtained. It is then drawn through a Jones Reductor to change all the iron to ferrous and titrated with N/10 potassium permanganate solution. The iron is calculated to Fe_2O_3 and the alumina determined by difference.

If manganese is present it is determined in a separate sample in a method given later and is subtracted from the iron in the above. In white enamels containing only a trace of iron the manganese may be determined in the solution from the pyrosulfate fusion. A freshly prepared solution of potassium ferricyanide is added to oxidize the manganese, then the solution is made alkaline with sodium hydroxide solution and the manganese-dioxide thus formed is filtered off. The solution is then made acid and the ferrocyanide is titrated with N/10 potassium permanganate solution. (1 cc. $KMnO_4 = 0.00435$ gram MnO.)

Calcium Oxide. The filtrate from the iron and alumina is raised to boiling, treated with boiling ammonium oxalate solution and digested on water bath until precipitate readily and quickly settles after being stirred. The calcium oxalate is now filtered off and ignited wet in platinum to constant weight over a strong blast.

Magnesium Oxide. The solution is evaporated to dryness and the residue ignited to remove ammonium salts. The residue is treated with a few drops of hydrochloric acid and taken up with boiling water and filtered from the carbonaceous residue. To the boiling solution is added drop by drop a solution of sodium ammonium phosphate

and is allowed to cool. Half as much concentrated ammonium hydroxide is added as there is solution and it is allowed to stand over night. The precipitate is collected on a filter, washed with 3% ammonia water, dried in oven and ignited separate from the filter. The heat is applied gently at first and finally with the highest heat of a good Bunsen burner. It is then weighed as $Mg_2P_2O_7$.

1 gram $Mg_2P_2O_7 = .3625$ grams MgO.

The alkalies are determined by the method of J. Lawrence Smith from a gram sample finely powdered. This method is standard and need not be given here.

Separation and Determination of Antimony, Tin. Manganese and Cobalt in Enamel.

Decomposition. Two grams finely powdered sample are transferred to a platinum dish, and after moistening with a little water, pure hydrofluoric acid is added and the whole is mixed with a platinum spatula. The dish is digested on steam bath for five hours covered with platinum cover (a larger platinum dish may be used for cover if no other is at hand). After the decomposition is complete the solution is evaporated to dryness on steam bath. The residue is moistened with enough dilute sulfuric acid (1:1) to make a thin paste, and evaporated as far as possible on a steam bath and then on a hot plate, all the time being covered to prevent spirting. As soon as fumes of sulfuric anhydride cease to be evolved the cover is strongly heated until fumes cease to be driven off, when it is removed. The contents are heated by bringing the dish to dull redness directly over a Bunsen burner. The sulfates thus formed are moistened with strong hydrochloric acid, a little hot water is added and the solution boiled with repeated additions of acid and water until completely in solution. In some enamels—especially those with high melting points—the stannic oxide remains un-

dissolved, and a fusion of the residue with sulfur and sodium carbonate as given later under "The Analysis of Oxide of Tin" may be necessary.

Treatment with H_2S. The solution containing at least 30 cc. double normal hydrochloric acid is transferred to a 500 cc. Ehrlenmeyer flask fitted with a double bored stopper. Through one of the holes a right-angled piece of glass tubing is introduced that just reaches to the lower edge of the stopper, while through another hole another right-angled glass tube is fixed so that it almost reaches the bottom of the flask.

A Kipp H_2S generator is connected to the longer tube and H_2S is passed through for half an hour and the solution is let stand for another half an hour, after which the sulfides of antimony and tin are transferred to a filter paper and the solution is kept for the determination of manganese and cobalt.

Antimony and Tin. The precipitated sulfides are dissolved in a solution of potassium polysulfide—if any lead or copper is present it will remain undissolved and may be determined separately—by pouring this successively through the filter into a 300 cc. Jena beaker, and finally washing with water containing a small amount of potassium polysulfide.

Antimony. The antimony and tin in this solution are separated by F. W. Clark's method as modified by F. Henz[1], as follows:

To the solution in the Jena beaker 6 grams caustic potash and 3 grams tartaric acid are added. To this mixture twice as much 30 per cent. hydrogen peroxide is added as is necessary to completely decolorize the solution, and the latter is now heated to boiling and kept there until the evolution of oxygen is over, in order to oxidize the thiosulphate formed. All of the excess of peroxide cannot be removed successfully at this point. The solution is cooled somewhat, the beaker covered with a watch-glass,

[1] Treadwell, Vol. II, p. 188.

and a hot solution of 15 grams pure recrystallized oxalic acid is cautiously added (5 gms. for 0.1 gm. of the mixed metals). This causes the evolution of considerable carbon dioxide. Now, in order to completely remove the excess of hydrogen peroxide the solution is boiled vigorously for ten minutes. The volume of the liquid should amount to from 80 to 100 cc. After this a rapid stream of hydrogen sulfide is conducted into the boiling solution, and for some time there will be no precipitation, but only a white turbidity formed. At the end of five or ten minutes the solution becomes orange colored and the antimony begins to precipitate, and from this point the time is taken. At the end of fifteen minutes the solution is diluted with hot water to a volume of 250 cc., at the end of another fifteen minutes the flame is removed, and ten minutes later the current of hydrogen sulfide is stopped. The precipitated antimony pentasulfide is filtered off through a Gooch crucible which, before weighing and after drying, has been heated in a stream of carbon dioxide at 300°C. for at least one hour. The precipitate is washed twice by decantation with 1 per cent. oxalic acid and twice with very dilute acetic acid before bringing it in the crucible. Both of these wash liquids should be boiling hot and saturated with hydrogen sulfide.

The crucible is heated in a current of carbon dioxide (free from air) to constant weight, and its contents weighed as Sb_2S_3.

The filtrate is evaporated to a volume of about 225 cc., transferred to a weighed unpolished platinum dish, and electrolyzed at 60° to 80°C. with a current of 0.2 to 0.3 ampere (corresponding to 2 to 3 volts). For very small amounts of tin, a current of not over 0.2 ampere should be used. At the end of six hours 8 cc. of sulfuric acid (1:1) are added, and at the end of twenty-four hours the solution is transferred to another dish. The deposited tin has a beautiful appearance, similar to silver.

Tin. The plated tin is washed thoroughly with water and the dish is dried in an air oven at 110° and weighed.

The solution containing the cobalt and manganese is boiled until free from H_2S. The iron is oxidized back to the ferric state by the addition of bromine water and boiling until the excess of the latter is expelled. Ten cc. double normal ammonium chloride is added and the iron and alumina are precipitated by the addition of ammonia and are filtered off. (The iron alumina may be determined from this precipitate if desired.)

The solution still containing the manganese and cobalt is transferred to an Ehrlenmeyer flask fitted for passing in H_2S, as before described, and 3 cc. strong ammonia is added. H_2S is passed through for some time, and after precipitation ceases 3 cc. more of ammonia are added and the flask is filled to the neck (300 cc. flask), is corked and set aside for twelve hours at least. The precipitate is collected and washed on a small filter with water containing amonium chloride and sulfide.

Manganese. The manganese is extracted from the precipitate on the filter by pouring through it strong H_2S water acidified with $\frac{1}{5}$ its volume hydrochloric acid (sp. gr. 1.11). This solution from the extraction is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drop of sodium carbonate solution, hydrochloric acid and a drop of sulfurous acid are added to decompose excess of carbonate and to dissolve the precipitated manganese, and the latter is reprecipitated at boiling heat by sodium carbonate after evaporating off the hydrochloric acid. The manganese is weighed as Mn_3O_4 and calculated to MnO_2, in which form it is probably present in the enamel.

The residue of cobalt sulfide left after extracting the manganese is burned in a porcelain crucible, dissolved in aqua regia, and evaporated with hydrochloric acid; the platinum—and copper if any is present—are thrown down by heating and passing in hydrogen sulfide. The filtrate from the platinum and copper is made ammoniacal, and cobalt is thrown down by hydrogen sulfide. This is filtered

off and washed with water containing ammonium sulfide. This is either ignited and weighed as oxide or more accurately determined by dissolving in an ammoniacal solution of ammonium sulfate, containing 10 grams of ammonium sulfate and 40 cc. of concentrated ammonia for each 0.3 grams of cobalt, and electrolyzing in a weighed platinum dish at room temperature with a current of 0.5 to 1.5 ampere, and an electromotive force of 2.8 to 3.3 volts. The electrolysis is finished in three hours. The circuit is broken and the liquid poured off, and the platinum dish is washed with water, then with absolute alcohol (distilled one hour) and finally with ether, allowed to dry in oven at 95° for one minute and then weighed. The metallic cobalt is calculated as CoO, in which form it is present in the enamel.

The Determination of Boric Anhydride in Enamel.

The boron is determined in a separate sample of about 0.3 grams. This finely pulverized sample is fused with three grams sodium carbonate for fifteen minutes, is taken up with thirty cc. dilute hydrochloric acid and a few drops of nitric acid. The melt is heated in a 250 cc. round-bottomed flask almost to boiling, and dry precipitated calcium carbonate is added in moderate excess. The solution is boiled in the flask after it has been connected with a six-inch worm reflux condenser. The precipitate is filtered on an 8 cm. Buchner[1] funnel, and is washed several times with hot water, taking care that the total volume of the liquid does not exceed 100 cc.

The filtrate is returned to the flask, a pinch of calcium carbonate is added and the solution is heated to boiling to remove the free carbon dioxide. This is best done by connecting the flask to a suction pump, and the suction is applied during boiling. The solution is cooled to ordinary

[1] See Method of Wherry and Chapin, Jr., Am. Chem. Soc. 30. p. 1688. for Determination of Boron in Silicates.

temperature, filtered if the precipitate has a red color, and four or five drops of phenolphthalein is added and N/10 sodium hydroxide solution is run in slowly until liquid has a strongly pink color. A gram of mannite (or 150 cc. of neutral glycerol) is added, whereupon the pink color will disappear. Continue to run in N/10 sodium hydroxide until end point is reached. Add more mannite or glycerol and if necessary more alkali, until a permanent pink color is obtained.

1 cc. N/10 Sodium Hydroxide = .0035 g. B_2O_3.

Lead. The enamel for cooking utensils should never contain lead. To determine whether a cooking utensil contains lead, E. Adam gives the following simple qualitative method: A small piece of filter paper moistened with hydrofluoric acid is placed upon the enamel and allowed to remain for some minutes; the paper, together with any pasty mass adhering to the enamel, is then washed off into a small platinum basin, diluted with water, and tested for lead by passing H_2S through the solution.

J. Grünwald (Oesterr. Chem. Ztg. 8, p. 46) gives another quick test for lead: Wet small portion of surface with HNO_3 (conc.) and heat until acid is evaporated. Add several drops of water and a few drops 10% potassium iodide solution, and if even a trace of lead is present yellow lead-iodide will be produced.

Determination of Phosphoric Anhydride in Enamel.

Enamels containing bone ash to give opaqueness are analyzed for P_2O_5 as follows:

To a gram sample of very finely pulverized enamel in a platinum crucible one cc. of sulfuric acid is added and the crucible is filled half full (about ten cc. are required) with hydrofluoric acid. The crucible is heated on the water bath until most of the solution is evaporated and then gently on a hot plate to remove all the fluorine as

silicon-tetra-fluoride and as hydrofluoric acid, but no sulfuric acid fumes should evolve, as P_2O_5 is volatile. The residue is dissolved in nitric acid and taken to dryness, moistened with nitric acid, diluted with water, filtered and washed with a very little water.

Add aqueous ammonia to the solution from above until the precipitate of calcium phosphate first produced just fails to redissolve, and then dissolve this by adding a few drops of nitric acid. Warm the solution to about 70°C. and add 50 cc. ammonium molybdate solution (70g. MoO_3 per liter). Allow the mixture to digest at 50° for twelve hours. Filter off precipitate washing by decantation with a solution of ammonium nitrate made acid with nitric acid.

The precipitate on the filter is dissolved by pouring through it dilute ammonia solution (one volume of 0.96 sp. gr. ammonia to three volumes of water).

The solution is received in the beaker containing the bulk of the precipitate, all of which is dissolved in the ammonia solution.

An excess of magnesium ammonium chloride ("magnesia mixture") solution is added very slowly and with constant stirring. Let solution stand over night. Decant clear solution through a filter and wash by decantation with ammonia water (1:3). Dissolve the precipitate by pouring a little hydrochloric acid (sp. gr. 1.12) through the filter, allowing the acid solution to run into the beaker containing most of the precipitate. When all the precipitate on the filter and in the beaker is dissolved wash the filter paper with a little hot water. To the solution add 2 cc. magnesia mixture and then strong ammonia, drop by drop, with constant stirring until distinctly ammoniacal. Stir several minutes then add strong ammonia equal to one-third of the liquid, let stand two hours and filter off the precipitate of magnesium ammonium phosphate. Wash with dilute ammonia water, dry the precipitate, ignite separately from the filter, first at low temperature and

gradually raise to full blast. Weigh precipitate as $Mg_2P_2O_7$ and calculate as P_2O_5 in sample.

PART II.

THE ANALYSIS OF ENAMEL RAW MATERIALS.

The Analysis of Borax.

Sampling. A handful is taken from the middle of every tenth bag as it is unloaded. The sample from the entire car-load is then quartered down to two pounds. This is crushed so that it will pass through a forty mesh sieve. This is further quartered to about thirty grams. Sample is then accurately weighed and thoroughly dissolved in about 600 cc. hot—not boiling—water in a liter volumetric flask, and when cool is diluted to the mark. One hundred cc. of this, representing one-tenth of the sample, is then taken for analysis.

Determination of Sodium Oxide and Boric Acid. Titrate with normal sulfuric or hydrochloric acid solution, using methyl orange as indicator.

Number cubic centimeters Normal Acid $\times$ .031 = g, Na_2O. The solution is now boiled, covered with a watch glass to expel CO_2, and on cooling may turn pink. Add normal KOH solution (a drop will do) to bring back yellow color. At this stage all the boric acid exists in a free state.

$$(2Na^+ + B_4O_7^{--}) + H_2O + (2H^+ + 2Cl^-) = (2Na^+ + 2Cl^-) + 4(H^+ + 4BO_2^-)$$

Add as much neutral glycerol as there is solution (about 150 cc.) and titrate with normal potassium hydroxide, using phenolphthalein as indicator. If end is not distinct add more glycerol and more indicator.. The addition of glycerol causes the boric acid to become more dissociated, probably due to the formation of boroglyceric acid, and the end-point is quite distinct. The following equation represents essentially what takes place:

$$(4H^+ + 4BO_2^-) + (4K^+ + 4OH^-) = (4K^+ + 4BO_2^-) + 4H_2O.$$

1 cc. normal KOH solution = .035 g. B_2O_3.

If the analysis gives more Na_2O than is required to calculate all the B_2O_3 to $Na_2B_4O_7$, the remainder comes from sodium carbonate with which it has been adulterated.

Calculation of Results. The analysis of the borax is very important, as many times samples are adulterated, and even when not adulterated seldom contain exactly enough water to give the formula $Na_2B_4O_7 \cdot 10H_2O$. It is necessary to know the strength of the borax not only to buy intelligently, but also so that each and every mix of enamel will contain the same amount of borax.

It is customary to calculate from the percent of B_2O_3 in sample the percent strength of the sample as $Na_2 \cdot B_4O_7 \cdot 10H_2O$.

$$\%B_2O_3 \times 2.7307 = \%Na_2B_4O_7 \cdot 10H_2O.$$

When the sample has dehydrated of course this will run over 100%, and thus the correspondingly fewer pounds of borax may be used in the mix of enamel.

Moisture. On account of the large amount of water of crystallization in borax it is difficult to determine the moisture directly, therefore it is calculated by subtracting the % $Na_2B_4O_7 \cdot 10H_2O$ and the % Na_2CO_3 (if any is present) from 100%.

The Analysis of Ground Sand, Flint and Quartz.

Fineness. These, as are most of the raw materials used in the enamel, are tested for fineness. One kilogram is weighed on balance sensitive to 1/10 gram and is shaken on a 100 mesh sieve. The material remaining on the sieve is weighed. This is then shaken on an 80 mesh sieve and the residue weighed. From this is calculated percent through 100 mesh and percent through 80 mesh. The finer the material the better it is for use in making enamel.

An analysis for SiO_2, Fe_2O_3 and MgO is run when a new material is being tried, but generally only the SiO_2 and Fe_2O_3 are determined. In this case the acid solution from the silica is reduced by passing through a Jones Reductor and is titrated with N/10 potassium bichromate.

Preparation for Analysis. The material is carefully sampled by quartering down to several grams. This is ground in an agate mortar to pass completely through a hundred mesh sieve. This grinding is generally done by hand but an enameling works laboratory should be equipped with a McKenna Grinder, (manufactured by McKenna Bros. Brass Company, Ltd., of Pittsburgh), in which the material can be ground in an agate mortar by power.

The method followed for the analysis of flint and other forms of silica as well as clays and feldspars, is in all essentials, a well known method given by Hillebrand in analysis of silicate rocks, U. S. Geological Survey Bull. 305, and for reasons of space this method will not be given here.

The Determination of Titanium in Enamels, Clays and Silicate Minerals.

Titanium is determined after the determination of the iron by titrating with permanganate. This solution (after titrating) is diluted to 1000 cc. and is treated with hydrogen peroxide and the titanium determined by A. Weller's Colorimetric Method,[1] from one-half the solution.

This determination depends upon the fact that acid solutions of titanium sulphate are colored intensely yellow when treated with hydrogen peroxide; the yellow color increases with the amount of titanium present and is not altered by an excess of hydrogen peroxide. On the other hand, inaccurate results are obtained in the presence of hydro-fluoric acid (Hillebrand); consequently it is not permissible to use hydrogen peroxide for this determination which has been prepared from barium peroxide by means of hydrofluosilicic acid. Furthermore, chromic, vanadic, and molybdic acids must not be present, since they also give colorations with hydrogen peroxide. The presence of small amounts of iron do not affect the reac-

[1] Berichte 15, p. 25-93.

tion, but large amounts of iron cause trouble on account of the color of the iron solution. If, however, phosphoric acid is added to the colored ferric solution it becomes decolorized, and from such a solution the determination of titanium offers no difficulty. The solution in which the titanium is to be determined must contain at least 5 per cent. of sulfuric acid; an excess does not influence the reaction. The reaction is so delicate that 0.00005 gm. of TiO_2 present as sulphate in 50 cc. of solution give a distinctly visible yellow coloration.

For this determination a standard solution of titanium sulfate is required. This can be prepared by taking 0.6000 gm. of potassium titanic fluoride which has been several times recrystallized and gently ignited (corresponding to 0.2 gm. of TiO_2). This is treated in a platinum crucible several times with a little water and concentrated sulfuric acid, expelling the excess of acid by gentle ignition, finally dissolving in a little concentrated sulfuric acid and diluting with 5 per cent. sulfuric acid to 100 cc. One cubic centimeter of this solution corresponds to 0.002 gm. TiO_2.

The determination proper is carried out in the same way as the colorimetric determination of ammonium in the sanitary analysis of water.

50 cc. of the solution which has been brought to a definite and accurately measured volume is placed in a Nessler tube beside a series of other tubes, each containing a known amount of the standard titanium solution, filled up to the mark with water and each treated with 2 cc. of 3 per cent. hydrogen peroxide[1] (free from hydrofluoric acid). The color of the solution in question is compared with the standards. This method is only suitable for the estimation of small amounts of titanium, as the shades of strongly colored solutions cannot be compared accurately.

[1] The hydrogen peroxide solution is prepared shortly before using by dissolving commercial potassium percarbonate in dilute sulfuric acid.

The Analysis of Oxide of Tin.

Stannic Oxide. As this is one of the most important and most expensive of the raw materials used in enameling, an analysis is very necessary. The oxide is bought to contain not less than 99.5% SnO_2, and in this the impurities will consist of minute traces only of other materials. For an oxide of this kind from .2 to .3 of a gram of the sample is placed in a porcelain casserole, about 10 cc. of C. P. nitric acid of a sp. gr. 1.2 is added and the solution is slowly evaporated to a volume of about 2 or 3 cc., diluted to about 30 or 40 cc. of water, kept warm for about a half hour, filtered on a small blue-ribbon filter paper, and washed with warm water, slightly acidulated with nitric acid, being careful to avoid letting the precipitate creep up.

The precipitate is dried on filter paper in the funnel by placing in a hot air bath. The dried tin oxide is then removed as completely as possible from the filter paper and the paper is ignited in a porcelain crucible, being sure that there is an excess of air so that there will be no metallic tin reduced.

The balance of oxide of tin is now added to the crucible and the whole is moistened with a drop of nitric acid, the temperature under the crucible is gradually raised until it comes to a bright red heat over the blast flame.

This method gives results which check within one-tenth of a per cent.

Some brands of oxide of tin on the market contain a number of impurities in considerable quantities. Lead, iron, silica, sodium chloride, sodium sulfate and water are the most common of these. These are determined as follows:

Direct Method. Methods for the direct determination of the tin have proven quite unsatisfactory but the following, with very careful manipulation, yields results checking within 0.2%:

Five-tenths grams of oxide is mixed in a porcelain crucible with 3 grams each of powdered sulfur and dry

carbonate of soda, which both of course must be C. P., especially free of metals and earths. The covered crucible is heated for about an hour at *low heat first,* and later at the heat of a regular Bunsen burner; then let cool without lifting the cover. The cold mass is dissolved in water, filtered and washed with water to which was added a little sulfide of ammonia; the residue is brought back in the crucible and the melting process repeated, of which the solution is filtered to the first melting. The sulfide tin solution then is acidulated with hydrochloric acid and the precipitated sulfide of tin is allowed to settle clearly, after which it is filtered and washed with sulfide of hydrogen water.

The wet precipitate of sulfide of tin is transferred to an Ehrlenmeyer flask and treated with dilute hydrochloric acid and bromine until completely dissolved, at a low heat. The filter left after the solution is filtered off is washed and the $SnCl_2$ solution is precipitated with ammonia and a little nitrate of ammonia, allowed to settle, filtered and washed. After drying, the precipitate is ignited at white heat and is weighed as SnO_2.

Reduction Method. When the qualitative analysis shows no metal other than tin present, a very satisfactory method is to reduce a weighed quantity of the sample in a Rose crucible by heating to redness in a stream of hydrogen. The silica, if any is present, may be determined by dissolving out the tin with hydrochloric acid and weighing the residue.

Combined Water. In oxides which are prepared by certain precipitation methods, the combined water runs as high as ten per cent. To determine this, a two gram sample is heated in a porcelain crucible at a white heat to constant weight. The loss is combined water.

Lead. The lead is determined from the nitric acid solution and washings from the tin oxide determination by precipitation as the sulfate.

Iron. Digest about one gram with twenty-five cc.

of concentrated hydrochloric acid. As much water is added and the solution is boiled for five minutes. The residue is filtered off and about a cubic centimeter of concentrated sulfuric acid is added and the solution is evaporated until the sulfuric fumes come off. The solution is diluted, passed through a Jones Reductor and titrated with N/10 potassium permanganate solution.

Soluble Salts. About two grams of the sample is boiled with water for thirty minutes. The residue is filtered on a blue-ribbon paper and is dried in an air bath. It is then separated as completely from the paper as is possible. The paper is burned in a platinum crucible. A drop of nitric acid is added and the crucible is raised to bright red. The whole of the residue is now added and heated to white heat for some time. (If there was combined water present in the sample of course it will be driven off, and this must be taken into calculation).

The loss in weight (minus the above correction) is the soluble salts—usually sodium chloride and sulfate.

If desired these may be determined definitely by usual methods. (Titration of an aliquot part with N/10 silver nitrate solution for the chloride and precipitation of the sulfate as barium sulfate in another aliquot part slightly acidifies with nitric acid.)

Silica. To the residue in the platinum crucible from the above determination several drops of sulfuric acid are added, and the crucible is filled within a quarter of an inch of the rim with pure hydrofluoric acid. This is volatilized, carrying with it any of the silica as hydrofluosilic acid. Loss of weight $= SiO_2$.

The Analysis of Pyrolusite.

Pyrolusite has two uses in enamel, first as an oxidizing agent, and second to give an amethyst color to the enamel frit. Its grading, however, is generally made on its oxidizing value. This is found as follows:

Manganese Dioxide. A sample is carefully taken

from each barrel of the shipment, and after quartering down to about ten grams is ground so as to pass through a 200 mesh sieve. (It is better to test this by seeing if any grit can be detected when the powder is placed between the teeth.) The sample is dried, spread out on a watch glass, at 110° for one hour, transferred to a stoppered weighing tube, and after weighing, about one-half gram is transferred into a 250 cc. Ehrlenmeyer flask. For each gram of sample weighed out add at least 0.9 grams *pure,* tested oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) weighing the acid accurately and recording the same. Add about 30 cc. of water and 30 cc. 5 normal sulfuric acid and drive off carbon dioxide by heating gently.

It is seldom necessary to filter after some practice, so the solution is titrated hot for the excess of oxalic acid with N/10 potassium permanganate solution. Calculate amount of oxalic acid oxidized by the pyrolusite. The reaction is

$$MnO_2 + H_2C_2O_4 \cdot 2H_2O + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O.$$

Each gram oxalic acid oxidized therefore corresponds to .6902 g. MnO_2.

As pyrolusite is added to some enamels only to give color it is sometimes necessary to know its coloring power, and this is dependent upon the total manganese.

Total Manganese. One-half gram sample is boiled with strong hydrochloric acid until chlorine ceases to be evolved. The solution is neutralized with calcium carbonate and an *excess* of a strong *filtered* solution of bleaching powder is added. The solution is boiled until deep red, then alcohol is added until the red color disappears. The whole of the manganese now exists as MnO_2 and may be reduced with oxalic acid and titrated for its oxidizing power as before with N/10 permanganate of potassium. Each gram oxalic acid oxidized corresponds to .4361 g. Mn.

The Analysis of Soda Ash and Pearl Ash.

Generally it is only necessary to determine the total alkali in a sample of either soda ash or pearl ash, and to calculate from this the percentage of Na_2O or K_2O. A more complete analysis includes the determination of insoluble matter, iron, chloride, sulfate and moisture, as well as the total alkali.

Insoluble Matter. 50 g. weighed on rough balance (sensitive to 0.1 g.) and sufficient water added to dissolve the ash, shaking until dissolved. After an hour's digestion the solution is filtered through a weighed Gooch crucible with a circle of filter paper covering the bottom. This is dried at 105° and the increase in weight is insoluble matter.

Iron. The iron in the above insoluble matter is dissolved by pouring hot dilute hydrochloric acid through the precipitate in the Gooch crucible. The iron is precipitated from this by ammonium hydroxide and filtered on a white ribbon filter paper. The still moist precipitate is dissolved in sulfuric acid, reduced by means of a Jones Reductor and titrated with N/10 permanganate.

Chloride. Three gram samples are dissolved in water and nitric acid added until the solution is neutral (test with litmus paper). It is then titrated with N/10 silver nitrate solution.

Sulfate. Five or ten grams are dissolved in hydrochloric acid and the sulfate precipitated from the almost boiling solution by the addition of hot barium chloride solution.

Total Alkali. Twenty-five grams are dissolved in water in a 500 cc. volumetric flask and 50 cc. are titrated with N. hydrochloric acid, using methyl orange as indicator.

Hydroxide. To 50 cc. from above, precipitate all the carbonate with barium chloride. Without filtering, add phenolphthalein and titrate until colorless with normal hydrochloric acid.

Moisture. Ten gram samples are dried at 120° for two hours.

The Analysis of Saltpeter and Chili Saltpeter.

Moisture. Ten gram samples are heated to constant weight in an air-bath at 130°.

Insoluble Matter. Twenty grams are dissolved in boiling water and filtered through a weighed Gooch crucible with a circle of filter paper on the bottom. After drying at 110° in air bath to constant weight, the increase in weight is the insoluble matter.

Chlorine. The solution from above—this should be about 500 cc.—is placed in a 1000 cc. volumetric flask and 25 cc. (representing 0.5 g. sample) is titrated with N/10 silver nitrate, using potassium chromate as indicator. The result is calculated to sodium chloride.

Sulfate. Twenty cc. are heated to boiling and precipitated by adding hot barium chloride solution, a drop at a time and with constant stirring. After two hours digestion (or until precipitate settles quickly after agitating), filter through a Gooch crucible with ignited asbestos filter, ignite and weigh as barium sulfate. This is calculated to calcium sulfate.

Calcium and Magnesium. From five hundred cc. of the above solution (equal to 10 grams sample) at boiling temperature precipitate the calcium as oxalate by the addition of ammonium oxalate, being careful not to add much excess, as magnesium is to be determined in the same sample. Filter on a white ribbon filter paper, after an hour's digestion on the steam bath, ignite wet paper in platinum crucible, gradually increase to full blast and heat to white heat to constant weight. Weight as calcium oxide.

Determine the magnesium in filtrate from the calcium by addition of a solution of microcosmic salt and afterward one-third the volume of concentrated ammonium hydroxide, added drop by drop. The precipitate, ignited

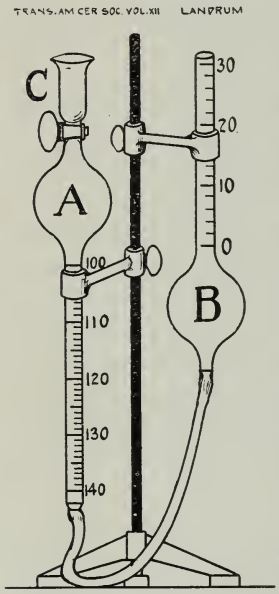
separate from the filter paper, is heated at first gently and at last with the full heat of a Bunsen burner, and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$).

Perchlorate. Ten grams of the sample of which the chloride content has already been determined, is mixed with an equal quantity of chemically pure sodium carbonate, and is heated in a large, covered, platinum crucible to quiet fusion. Ten or fifteen minutes are required. The product is then dissolved in nitric acid and the chloride estimated as usual.

Nitrogen. This is determined by the Kjeldahl method after reducing the nitrate to ammonia. Twenty grams of the sample are ground coarsely and dissolved in water in a liter flask, and solution is diluted to the mark. Twenty-five cc. (equal to 0.5 g. sample) of this solution is mixed in a 800 cc. Kjeldahl flask with 15 cc. concentrated sulfuric acid to which 2 grams salicylic acid have been added, then add gradually 2 grams zinc dust and shake flask to mix contents. Digest over low flame with neck of flask slightly inclined until danger of frothing has passed. Increase flame until the acid boils briskly and until white fumes cease to come off. This usually takes about ten minutes.

Add .7 gram mercuric oxide and continue boiling, adding acid if necessary to keep solution from solidifying. Solution should be clear in a short time. Complete oxidation by adding a little powdered potassium permanganate and allow the contents to cool. Add about 200 cc. ammonia-free water and 25 cc. potassium sulfide solution (40 g. commercial salt to the liter) and shake thoroughly. Add several pieces of granulated zinc and then pour carefully down the side of the neck 100 cc. sodium hydroxide solution (500 g. per liter), avoiding shaking and thereby mixing the acid and alkali. After washing the neck with ammonia-free water connect the flask immediately with a previously set up block tin condenser, which has been thoroughly washed and the tips of whose delivery are im-

mersed in 30 cc. standard acid solution (half normal), colored with methyl orange contained in a 150 cc. Phillip's flask. Mix contents of digestion flask by shaking thoroughly, then heat carefully, then slowly (taking about an hour) distill over 200 cc. of the liquid. Titrate excess of acid with standard half normal alkali solution, and from this calculate percentage of nitrogen in sample.



Lung Nitrometer Method. Where frequent analyses are made the Lung[1] Nitrometer method is better. A nitrometer modified especially for the use of the determination of nitrate in saltpeter is here illustrated. The Nitrometer "A" and the leveling tube "B" are filled with mercury. From a twenty gram sample which has been dried at 110° to constant weight as nearly as is possible 0.35 grams is put into a weighing tube. This is then accurately weighed and the contents shaken into the entry tube "C." The weighing tube is again weighed and the difference in weight is the grams sample employed. This should be close to 0.35 grams so that the gas evolved will be more than 100 cc. and less than 130 cc. at ordinary temperature and pressure.

About .5 cc. water is then poured in and the solution and crystals (after a minute's standing) are drawn into the measuring tube by opening the three-way cock into the entry tube "C" and lowering the leveling bulb cautiously. The cup is washed, using less than 1 cc. of water, and about 15 cc. of strong sulfuric acid is admitted through the entry tube into the measuring tube. (More than 1½ cc. H_2O renders the acid too dilute, and the

[1] Berichte 1885, 18, 1391.

mercury is attacked). After the cock is closed the leveling tube is placed in a clamp, the measuring tube is thoroughly shaken and the following reaction takes place:

$$NnO_2+H_2C_2O_4 : 2H_2O+H_2SO_4 = MnSO_4+2CO_2+4H_2O.$$

The measuring tube is now placed in clamp on a level with the levelling tube and solution is allowed to cool for an hour.

The tube is then accurately leveled, allowing one division of mercury for each six and one-half divisions of acid, and the gas volume read off. The temperature and barometric pressure are read and the gas corrected to standard conditions. Each cc. NO gas corresponds to .0037986 g. $NaNO_3$ or .003845 g. KNO_3.

The Analysis of Cryolite.

Cryolite is a mineral occurring in large quantities in Greenland, and is the sodium salt of hydrofluo-aluminic acid, Na_3AlF_6. It is used in enamels and is fused, finely ground with the frit giving it a milky opaqueness which enamellers call "body." It is a very expensive material and is most always far from pure, either being deliberately adulterated or merely naturally impure.

Methods used by most chemists for its analysis are at the best crude. The direct determination of the fluorine is the only satisfactory means of properly grading it. The method used for cryolite is exactly the same as that employed in the analysis of fluorine-bearing enamel as given in the beginning of this article, except that one gram of the cryolite is finely ground with about three grams (accurately weighed) of pure silica, and this mixture is fused with about eight grams of equal parts of sodium carbonate and potassium carbonate. In determining the silica in the cryolite, this silica which has been added must be deducted from that found.

The alkalies are determined by the method of J. Lawrence Smith[1] from a gram sample finely powdered.

Combination of Results. All soda is combined with sufficient fluorine to form sodium fluoride (NaF_2). The remainder of the fluorine is combined with aluminum as aluminum fluoride (AlF_3). The remainder of the aluminum is calculated as alumina (Al_2O_3).

The Analysis of Fluospar.

Fluorspar is analyzed especially for its fluorine content by the same method as that given under Cryolite. It is a material seldom adulterated and a mere fusion with six times the weight of sodium carbonate, the taking to dryness with hydrochloric acid as in ordinary silicate analysis, the removal of iron and alumina as hydroxide with ammonia, and the precipitation with ammonium oxalate of the calcium and its final weighing as calcium oxide, is sufficient in most cases. All the calcium may be calculated as CaF_2. The determination of the fluorine, however, is of course the only exact method of accurately grading this material.

The approximate method for determining the fluorine is as follows:

Approximate Method for Fluorine. About one gram of sample finely ground and accurately weighed is intimately mixed in agate mortar with about the same quantity of pure silica. The whole is transferred to a 250 cc. Ehrlenmeyer flask—rinsing the mortar with more silica. The flask is weighed and a weighed quantity of concentrated sulfuric acid is added. The record should now show the weight of flask, silica and acid. The flask is gently heated and the loss of weight is calculated as silicon fluoride.

Iron. For use in light colored enamels the iron content of the fluorspar is important. Five grams, finely

[1] Am. Jour. Science (2) 50, p. 269. Treadwell-Hall Anal. Chem., Vol. II, p. 394.

ground, are heated in a platinum dish with an excess of sulfuric acid as long as hydrofluoric acid is given off.

After cooling it is diluted with 100 cc. of water, and after reducing by drawing through a Jones Reductor the solution is titrated with N/10 potassium permanganate solution.

Accurate Method for Fluorine. The fluorine may be accurately determined by the following method:

One gram sample (ground to pass through 200 mesh sieve) is mixed with three grams silica and three grams each sodium carbonate and potassium carbonate in a platinum crucible. *Heat gradually* until it is in quiet fusion. The thin liquid fusion soon changes to a thick paste or only sinters somewhat. The reaction is complete when there is no further evolution of carbon dioxide.

After fusion the melt is treated with water and after cooling the insoluble residue is filtered off and thoroughly washed. The solution contains all fluorine and considerable silica. Remove the silica by adding four grams solid ammonium carbonate. Heat liquid at 40°C. for some time and let stand over night. Filter in morning and wash with ammonium carbonate water.

Evaporate on water bath almost to dryness in platinum dish (keep covered, as liquid foams). Dilute with a little water. Add a few drops of phenolphthalein. Add dilute HCl until colorless. Heat on steam bath and color will return. Cool and repeat operation until 1.5 cc. double normal HCl is sufficient to make colorless. Remove last traces silica by treating the solution with a solution of moist zinc oxide in ammonia water. Boil until ammonia is completely expelled. Filter off silica and zinc oxide and wash with water.

Precipitate fluorine as calcium fluoride and calcium carbonate by adding an excess of calcium chloride. Filter, using blue ribbon paper, and wash thoroughly with hot water. Dry precipitate on funnel. Transfer as much as possible to a platinum crucible. Burn filter and add ash. Ignite contents of crucible.

After cooling the mass is covered with a slight excess of dilute acetic acid (this changes the calcium oxide to soluble acetate.) Evaporate to dryness on steam bath. Take up with water. Filter, wash and dry. Transfer most of precipitate to weighed platinum crucible. Burn filter paper. Add ash. Ignite and weigh as calcium fluoride, CaF_2. To confirm the results add cautiously little concentrated sulfuric acid. Evaporate off excess sulfuric acid, ignite and weigh as calcium sulfate.

The Analysis of Oxides of Antimony.

Arsenic. One gram of oxide of antimony is dissolved in 10 cc. of strong hydrochloric acid—at as low a temperature as possible. The solution is then cooled and packed in ice and the arsenic, which is almost invariably present, is removed by passing through H_2S for several hours. The As_2S_3 is filtered off in a weighed Gooch crucible, washed first with CS_2 and alcohol then with concentrated hydrochloric acid and dried at 100°, and weighed as As_2S_3.

Antimony. The filtrate from above is put into 250 cc. volumetric flask, rinsing the beaker well with concentrated hydrochloric acid and an equal part of water. All the H_2S is removed by passing through a current of air. Five grams of tartaric acid are added and the liquid diluted to the mark.

Twenty-five cc. of the solution are measured out with a pipette and are neutralized with dry sodium bi-carbonate—keeping covered to avoid loss—finally a pinch of sodium bi-carbonate and a cubic centimeter of clear starch solution is added and the mixture is titrated with N/10 iodine solution.

1 cc. N/10 Iodine = 0.0060 grams Sb.

The Analysis of Oxide of Cobalt.

Arsenic. One gram finely pulverized sample is fused at low heat with ten grams bisulfate of potassium for three

hours. The melt is extracted with water acidified with sulfuric acid and the arsenic is precipitated from the warm acid solution with H_2S, collected in a weighed Gooch crucible, washed with water containing H_2S and dried at 100° for one hour and weighed as As_2S_3.

Cobalt. The filtrate from above is boiled, and at the same time air is drawn through to remove the H_2S, and it is then treated by Fisher's Potassium Nitrite method[1] to separate the cobalt and the nickel.

The concentrated solution containing salts of both metals is treated with pure potassium hydroxide to alkaline reaction, made slightly acid with acetic acid, and to this a concentrated solution of pure potassium nitrite that has been made slightly acid with acetic acid is added. After vigorous stirring, the mixture is allowed to stand twenty-four hours in a warm place. Before filtering, a little of the clear solution is pipetted off and treated with more potassium nitrite to see if the precipitation of the cobalt has been complete. If a precipitate is formed, the whole solution is treated with more potassium nitrite and again allowed to stand until complete precipitation is effected. The precipitate is then filtered and washed with a barely acid 5 per cent solution of potassium nitrite until 1 cc. of the filtrate, after being boiled with hydrochloric acid and treated with caustic potash and bromine water, no longer gives a black precipitate of nickelic hydroxide. The cobalt precipitate is then transferred to a porcelain dish, covered, and hydrochloric acid is gradually added until there is no further evolution of nitric oxide, and after filtering, the cobalt is precipitated by means of caustic potash and bromine water.

The precipitate is filtered off, using blue ribbon filter paper, dried, and ignited. After cooling it is treated with water in order to remove the small amount of alkali which is always present, after which the residue is ignited in a stream of hydrogen and weighed as metal. After weigh-

[1] Treadwell, Vol. II, p. 130.

ing, the metal is disolved in hydrochloric acid, evaporated to dryness, the dry mass moistened with hydrochloric acid, then treated with water, and the small residue of silicic acid is filtered off. This residue is ignited and its weight subtracted from that obtained after the ignition in hydrogen.

Nickel. The filtrate containing the nickel is treated with hydrochloric acid until the nitrite is completely decomposed, and the nickel is precipitated with potassium hydroxide and bromine water as brownish-black nickelic hydroxide [$Ni(OH)_3$.]

The precipitate—which seldom contains more than ten milligrams of nickel—is washed with hot water, collected on a filter and is dried, ignited separately from the filter, and weighed as NiO, in which form it was probably present in the oxide.

Steel Plate.

The steel best adapted for enameled ware is of very low carbon value and extremely low in the other impurities, in fact, the nearer pure iron the better. Of the steel plate used by the Columbian Enamelling and Stamping Company, the best satisfaction was obtained from those giving the following analysis:

Sulfur from .040% to .050%; phosphorous from .030% to .090%; silica less than .01%; manganese from .060% to .040%, and carbon less than 0.10%. The sheets must be of an even gauge for seamless drawn work and of a dark soft quality, which allows them to be drawn without tearing. When the vessel is made without drawing and sheets are used flat, this evenness of gauge is not so much of object. The grain in all cases must be as open as possible. The sheet must be low in carbon and sulfur, as these develop gases at temperatures of the muffle, which would cause the enamel to peel off.

Samples of the steel plate are obtained from drillings taken from eight or ten sheets stacked in a pile, and

drilled holes are run every two inches on the diagonal of the plate. Drillings are sampled down to twenty-five grams, which are kept in stoppered bottles. The method of analysis is that commonly employed by steel-works chemists, and can easily be found in print elsewhere, and for that reason will not be given here.